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## Preventing Metal Corrosion from Emulsifiable Ethylene

Dibromide Packaged for Bark Beetle Control<sup>1</sup>R. H. Nagel<sup>2</sup>

Experiments with emulsified insecticides to kill bark beetles in pine and spruce indicated ethylene dibromide to be the most effective of five fumigants.<sup>3 4</sup> Use of an emulsion reduced handling and transportation because only the emulsifiable concentrate -- 20 percent of the emulsion volume -- had to be shipped to the infested Forest, where water is readily obtained from streams and beaver ponds.

For spruce beetle control, a field-size batch of emulsion was formed by mixing 4

<sup>1</sup> Assistance of R. D. Chisholm who suggested additives and helped design storage tests in 1952 is gratefully acknowledged. Dr. Chisholm, who retired December 31, 1962, was chemist, Entomology Research Division, Agricultural Research Service, U. S. Department of Agriculture, Moorestown, New Jersey.

<sup>2</sup> Entomologist, Rocky Mountain Forest and Range Experiment Station, with central headquarters maintained at Fort Collins, in cooperation with Colorado State University.

<sup>3</sup> Massey, C. L., Chisholm, R. D., and Wygant, N. D. Ethylene dibromide for control of Black Hills beetle. *Jour. Econ. Ent.* 46: 601-604. 1953.

<sup>4</sup> Massey, C. L., Chisholm, R. D., and Wygant, N. D. Chemical control of the Engelmann spruce beetle in Colorado. *Jour. Econ. Ent.* 46: 951-955. 1953.

gallons of water with 1 gallon of an emulsifiable concentrate containing, percent by weight, 34 ethylene dibromide, 5.6 emulsifier, and 60.4 solvent (No. 2 fuel oil). When this formula was released to control agencies in 1952, the storage life of the concentrate had not been evaluated. It was hoped that supplies would be prepared and applied while fresh; that is, soon after mixing, or, at most, before the end of the control season. For one reason or another, however, stocks are often carried over for several seasons. Deterioration of the emulsifiers, phase separation during subzero temperatures, and corrosion of storage containers occur when this product has to be stored for use the following season.

Of several suggested methods advanced for dispensing the concentrate to treating crews by the gallon, refillable gallon cans proved to be both popular and practical during the 1952 field trials. For crewmen, the gallon can provided a simple, handy, time-saving, and non-hazardous way to transfer a measured gallon of concentrate into "jeep" cans when forming 5-gallon batches of emulsion. Whether loaded or empty, the gallon cans handled easily and, in cartons of 6, were readily loaded and moved by truck or pack animal. Unfortunately, their tin lining corroded rapidly.



While they still used the cans and appreciated their usefulness, several control operators expressed the hope that corrosion could be inhibited. With that objective, storage-life evaluations were started on October 30, 1952. The evaluations produced an effective and relatively economical means for preventing corrosion in metal containers. The purpose of this paper is to present a brief account of the work and the improved formulation.

### Materials and Methods

Because corrosion inside steel and tin storage containers was believed to be caused by bromine and hydrobromic acid -- hydrolytic products of the ethylene dibromide molecule -- experimental lots of concentrate were treated with acid acceptors, and their effects on corrosion and emulsifiability studied. Two acceptors were used, epichlorohydrin and glycidyl phenyl ether, each at exploratory rates of 0.6 (0.05 lb./gal.), 1.2, and 2.4 grams per 100 milliliters of formulation. In three replicates, screw-top pint cans, manufactured of light, medium, or heavy tinplate, were then partially filled (400 ml.) with experimental concentrates. One group of these cans was stored on shelves at room temperatures, another at a constant oven temperature of 54°C. At the same time, a series of epichlorohydrin mixtures in Erlenmeyer flasks was also stored in the oven, each flask with strips of drum steel and tinplate.

### Results and Conclusions

In the cans stored at room temperature, both acceptors, even at the lowest concentra-

tions, prevented tin corrosion until the tests were concluded 7.2 years later. In contrast, the light-weight tin in the controls exhibited only fragments of tinplating at the end of 6 months.

For unknown reasons, the accelerated test method produced illogical effects. No treatment inhibited deterioration of emulsifiability.

Only because its market quotations have been lowest of the two acceptors tested, epichlorohydrin is suggested for preventing corrosion in storage containers.

As revised to include epichlorohydrin, the finished spruce beetle concentrate contains the following ingredients per gallon of formulation at 20°C. (68°F.):

	<u>Pounds per gallon</u>	<u>Percent by weight</u>
Ethylene dibromide (commercial)	3.00	33.7
Triton X-151 <sup>5</sup>	.08	.9
Triton X-171 <sup>5</sup>	.42	4.7
Epichlorohydrin	.05	.6
No. 2 fuel oil (0.77 gal. to make volume)	5.35	60.1

<sup>5</sup> Of the rather limited number of emulsifiers evaluated, three blends of Tritons (Rohm & Haas, Philadelphia, Pa.) produced the most satisfactory emulsions. Blended by weight, they are X-100 and B-1956, 3:5; X-151 and X-171, 1:5; and X-152 and X-172, 1:7. Because they pour at lower temperatures, a convenient property when preparing concentrate on the Forest, and have been available at lower prices, the use of Tritons X-151 and X-171 has been favored.